TEMPERATURE DEPENDENT MOLECULAR DYNAMICS SIMULATION STUDY OF [BMIM][Cl]

A dissertation

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by

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CERTIFICATE

This is to certify that the dissertation entitled, **"Temperature Dependent Molecular Dynamics Study of [bmim][Cl] "** submitted by **Ms. Vijayalaxmi Sahoo** for the award of Master of Science in Chemistry during the period of August 2013-May 2014 in the **Department of Chemistry, National Institute of Technology, Rourkela,** is a record of authentic work carried out by her under my supervision. To the best of my knowledge, the matter embodied in this dissertation has not been previously submitted for any degree in this/any other Institute.

May, 2014
Rourkela

Dr. Madhurima Jana

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Vijayalaxmi Sahoo

ABSTRACT

Atomistic molecular dynamics simulations of 1-Butyl-3-methylimidazolium chloride ([bmim][Cl]) were carried out at three different temperatures. Modelling of ionic liquids is quite tricky and requires systematic approach. The model reported here has been parameterized based on Antechamber code of AMBER force-field. Multinanosecond trajectories were generated to analyze the properties of the compound. Attempt has been made to compare the results obtained from simulation with the available experimental data. Our model has been proven to establish good correlation between them. The density of the modeled compound is found to very close to the available experimental data. Further, the structure of the compound has been analyzed by calculating radial distribution functions. The effect of temperature on these properties also explored. The results obtained from the simulations are found to correlate well with the data obtained from the X-ray scattering study.

CONTENTS

1. INTRODUCTION

Room temperature ionic liquids (RTILs), a new class of ionic salts have attracted attention of many researchers due to their potential applications in vivid field like electrochemistry[1], separation[2], catalysis[3,4] etc. These compounds are liquid at or around room temperature and have interesting physical and chemical properties. These compounds have very negligible vapor pressure due to strong Columbic interactions. They are termed as environmentally favorable "green solvents" due to their non-volatility, thermal stability and recyclable properties. Such properties make them suitable for industrial applications [5-6]. However, it can be noted that before an IL is being used in application it is essential to know its physical properties[7] and hence development of systematic method of selecting ion pairs prior to designing a new ionic liquid is essential.

Due to a large number of possible potential applications of RTILs, several experimental and theoretical studies were carried out from the last few years[8-12]. ILs usually consist of asymmetric organic cations such as imidazolium or pyrrolidinium cations and inorganic or organic anions, including Cl^-, Br^-, NO_3^-, BF_4^-, PF_6^-, etc. Physical properties of these compounds were investigated by the researchers over a long range of temperature and pressure[13]. Various sophisticated experimental techniques such as X-ray diffraction, NMR spectroscopy, IR and Raman spectroscopy, neutron diffraction etc. have been used to study the structural and dynamical properties of the compounds. Among the ILs compound containing 1-*n*-Butyl-3-methylimidazolium as cation is one of the mostly studied. Sloutskin et.al[14] reported the density increases by around 10-12 % at the [bmim][PF_6]$^-$ vapor interface as compared to that in the bulk. Blanchard and Brennecke[15] studied the density of pure [bmim][NO_3] at different pressure and temperature. Viscosities and densities of these compounds were measured by Seddon et.al. at various temperatures[16]. Their study further shows that the presence of chloride ions has large effect on physical properties of this ILs[17]. Using Raman spectroscopy Hayashi et al. [18] studied the properties of [bmim][Cl] in a greater extent. In a recent study Cummings and co-workers[19] have shown the effect of alkyl chain length and temperature on structural properties of pyrrolidinium based ionic liquid by using small angle X-ray scattering study.

Besides various sophisticated experimental techniques numerous theoretical and simulation methods have been developed to describe the properties of ILs. In this regards, it

should be mentioned that computer simulation is a powerful tool to study the microscopic properties of chemical systems. From simulated trajectories one can measure several properties which can be directly compared with suitable experiments. Thus the method acts as a bridge between models and theoretical predictions as well as between models and experimental results. A number of computational studies were carried out to understand the intermolecular structure and dynamics of ILs[20,21]. Thermodynamic properties of ILs such as density[22,23], self-diffusion co-efficient of ions[24-26], heat of vaporization[27] etc. were calculated by molecular dynamics (MD) simulations and were compared with experimental data. The structure of planar liquid-vapour interface of RTILs was explained by using atomistic MD simulations[28]. Beside simulation studies, researchers have used quantum chemical studies based on first principle technique. The method has generally applied to obtain the structure of ion-pairs[29,30]. An emperical method known as quantitative structure-property relation has been used to predict properties like melting point, toxicity of ILs[31,32]. However, the intrinsic relation between structure and property can only be revealed by using MD simulation techniques.

2. OBJECTIVES

Success of MD simulations in terms of predicting properties are often dependent on the intra-and inter-molecular potential functions which is popularly known as force-field. AMBER[33], CHARMM[34], OPLS[35] etc are widely known for modelling of various compounds. However, modelling of RTILs is quite tricky and requires systematic approach. In this work, attempt have been made to model [bmim][Cl] compound by using Antechamber code of AMBER force-field[33]. It should be noted that beside industrial applications experimental studies showed that this compound has been proven to stabilize protein's native state. Hence proper modelling of such compound would be of great interest. In Figure 1 we have shown a schematic diagram of the compound.

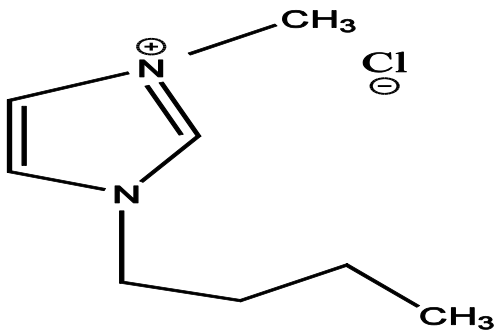

Figure 1: Schematic diagram of the compound [bmim][Cl].

Fine tuning of the model was done by performing long MD simulations at various temperatures. Further, effect of temperature on this model compound has been revealed by calculating the density and pair-wise correlation function. We have discussed these elaborately in the following Sections.

3. SYSTEM SETUP AND SIMULATION DETAILS

Three separate simulations of 100 ion-pairs were carried out using NAMD code[36] at three different temperatures such as 293K, 300K, 308K. In rest of the thesis we will refer these simulations as S1, S2 and S3. We have parameterized [bmim][Cl] compound using Antechamber code as implemented in AMBER[33]. The potential form as implemented in AMBER[33] can be expressed by the following expression,

$$E = \sum_{bonds} K_r(r - r_0)^2 + \sum_{angles} K_\theta(\theta - \theta_0)^2 + \sum_{dihedrals} \frac{K_\varphi}{2}\left[1 + \cos(n\varphi - \gamma)\right] + \sum_{i<j}\left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{r_{ij}}\right] \quad \textbf{(1)}$$

The first three terms describes the bonded interactions, i.e., bonds, angles and torsions. The last term gives the non-bonded interactions, including van der Waals (VDW, in the Lennard-Jones

(LJ) 6-12 form) and Coulombic interactions of atom-centered point charges. Electrostatic and VDW interactions are calculated between only the atoms in the same molecule separated by at least three bonds or the atoms in different molecules. The non-bonded interactions with separation of exactly three bonds (1-4 interactions) are reduced by a scale factor, which is optimized[33] as 1/2 for VDW and 1/1.2 for electrostatic interactions. Here, the LJ 6-12 potential is written as

$$E_{LJ} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] = \epsilon_{ij}\left[\left(\frac{\sigma_{min,ij}}{r_{ij}}\right)^{12} - 2\left(\frac{\sigma_{min,ij}}{r_{ij}}\right)^{6}\right] \qquad (2)$$

Where, ϵ_{ij} is the traditional well-depth. $ó_{ij}$ and $ó_{\min,ij}$ are the distances between atoms *i* and *j*, at which the energy of the two atoms reaches zero and minimum, respectively. Comparing eq (1) and eq (2), we get

$$A_{ij} = 4\epsilon_{ij}\,\sigma_{ij}^{12} = \epsilon_{ij}\,\sigma_{min,ij}^{12}\,; B_{ij} = 4\epsilon_{ij}\,\sigma_{ij}^{6} = 2\epsilon_{ij}\,\sigma_{min,ij}^{6} \qquad (3)$$

The LJ parameters for unlike atoms can be obtained from the Lorentz-Berthelot (LB) combining rule

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}\,; \sigma_{ij} = \left(\sigma_{ii} + \sigma_{jj}\right)/2 \qquad (4)$$

All the simulations were performed with periodic boundary conditions in a cubic box with side length 30.0 Å. The initial system was prepared by using packmol code[37]. The cubic box contained 200 [bmim][Cl] molecules (100 molecules of bmim and 100 molecules of Cl). The systems were first minimized using the conjugate gradient energy minimization method. Then gradually the temperature of each system was increased to the room temperature of 300 K within a short MD run. This was carried out at a constant pressure (P=1 atm) under the isothermal-isobaric ensemble (NPT) conditions. It was then followed by an NPT equilibration run at all the

three different temperatures 293K, 300K, 308K for 15ns duration for each of the systems. The temperature and pressure of the systems was controlled by Langevin dynamics and Nose–Hoover Langevin piston methods[38]. The cell volumes were allowed to fluctuate isotropically during this period. At the end of these NPT runs, the volumes of the three systems attained steady values with cell edge lengths 31.03, 31.03 and 31.03 Å for S1, S2 and S3 simulations. The dimensions of the simulation cells were then fixed and the conditions were changed to constant temperature and volume (NVT ensemble). After 20 ns, a NPT production run of 30 ns was carried out for each of the three systems. The average temperature of S1, S2 and S3 simulations are found to be 292.80 K, 299.47 K, 306.59 K respectively. MD time step of 1 fs was employed for each of the simulations and the trajectories were stored every 500 fs for subsequent analysis.

The minimum image convention[39] was employed to calculate the short range Lennard-Jones interactions using a spherical cut-off distance of 12 with a switch distance of 10. The long-range electrostatic interactions were calculated by using the particle-mesh Ewald sum (PME) method[40].

4. RESULTS AND DISCUSSIONS

In Figure 2 we have shown the snapshots of the initial and simulated [bmim][Cl] box as obtained from the different simulations, S1, S2, and S3 respectively.

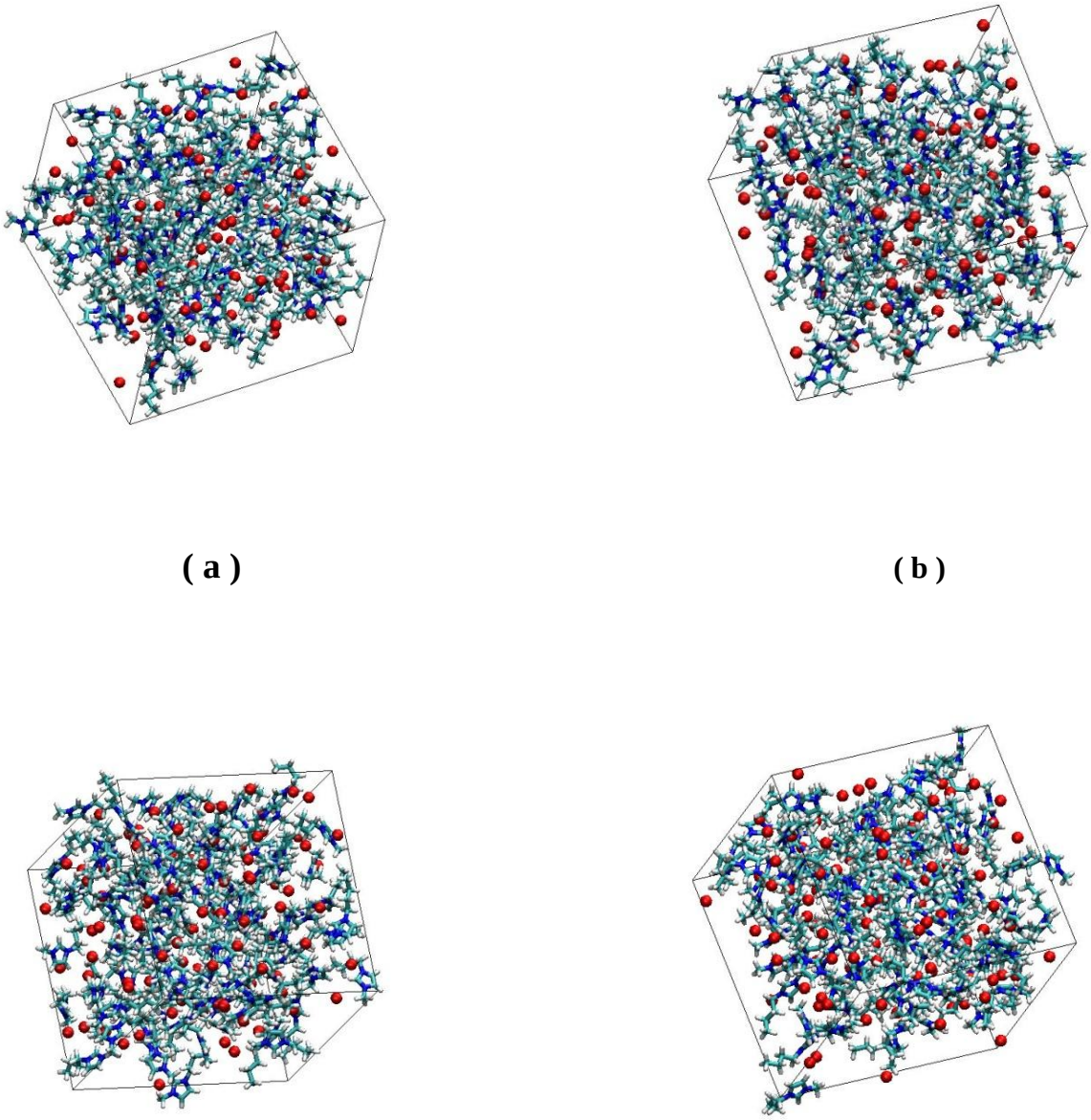

Figure 2: (a) Initial configuration of the [bmim][Cl] box and snapshots as obtained from the simulations (b) S1, (c) S2, and (d) S3 respectively. The $bmim^{+}$ molecules are shown in licorice and the Cl^{-} in red.

4.1 Temperature, Edge length and Energy

The time dependent variation of temperature, boxlength and energy as obtained from the three simulations, S1, S2, and S3 are shown in Figure 3, 4 and 5 respectively.

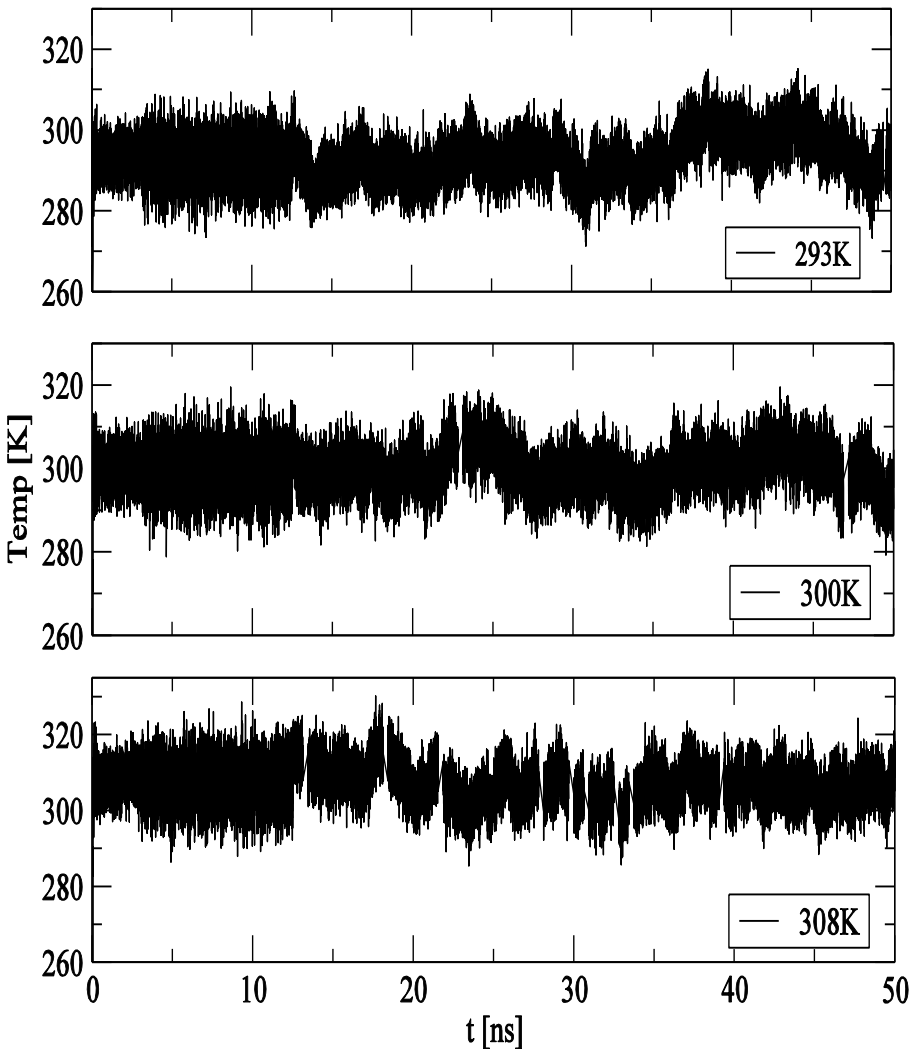

Figure 3: Temperature of the system as a function of time for the three simulations, S1, S2 and S3.

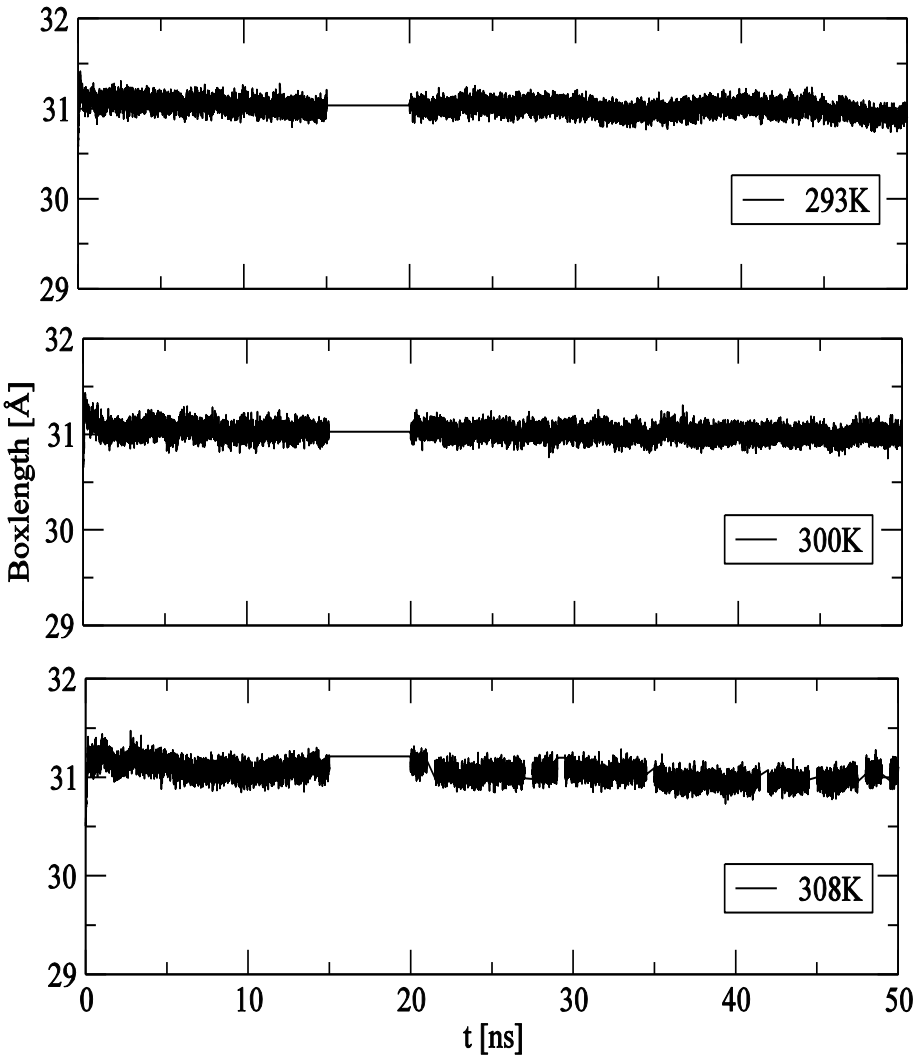

Figure 4: Boxlength of the system as a function of time for the three simulations, S1, S2 and S3.

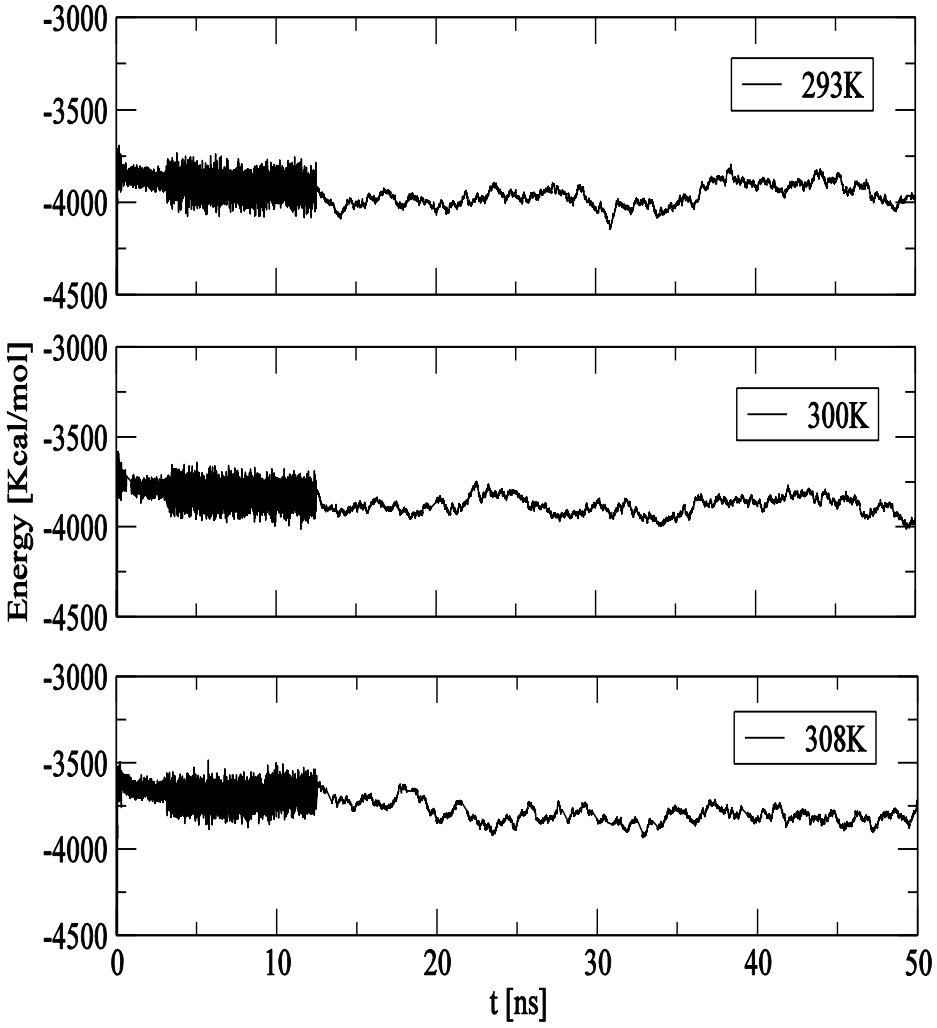

Figure 5: Energy of the system as a function of time for the three simulations, S1, S2 and S3.

All the plots clearly demonstrate that the systems are well equilibrated. The average temperature of the system for the three simulations, S1, S2, and S3 are found to be 292.8K, 299.47K, 306.59K, respectively. It is noticed that with increase in temperature the total energy of the systems increases which is quite expected.

4.2 Densities of Ionic Liquids

The density of the [bmim][Cl] ionic liquid obtained by the MD simulation at the three different temperatures, 293K, 300K and 308K is shown in Figure 6.

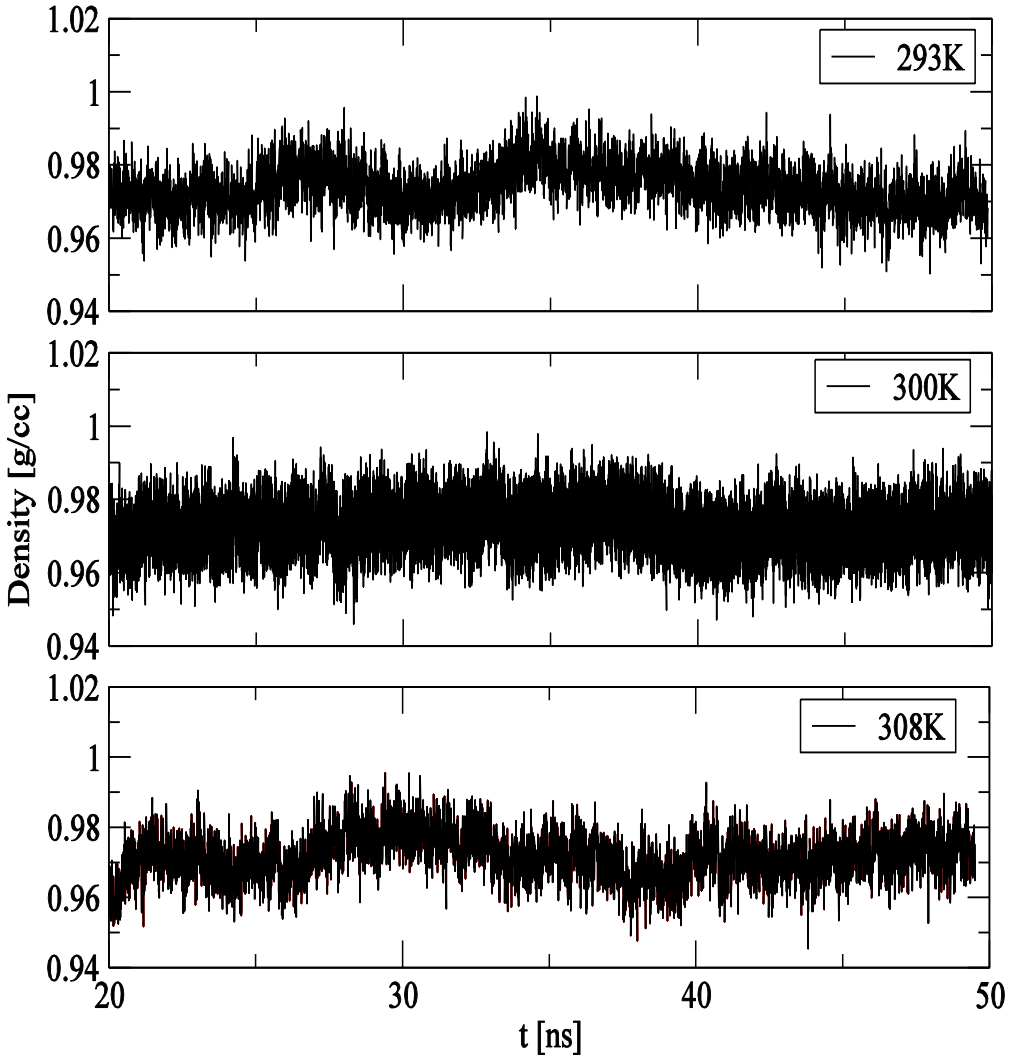

Figure 6: Density of [bmim][Cl] at three different temperatures for production runs as a function of time.

We have calculated the average densities at the three temperatures and have shown in Table 1. The experimental density of the [bmim][Cl] has given in the table for comparison.

Table 1: Densities of [bmim][Cl] as obtained from the simulation. The experimental density is also given for comparison.

Temperature (K)	Calculated (g/cc)	Experimental[41] (g/cc)
293	0.973	1.086
300	0.972	-
308	0.970	-

It is found that for the small change in temperature (within 20K) the density of the compound remains almost same however slight decrease in density is found as the temperature increases. Further the density of the compound as obtained from the simulation are found to be in good agreement with the experimentally available density.[41]

4.3 Structure of [bmim][Cl]

The radial distribution functions (RDF) for the cation-anion (C-A), cation-cation (C-C), anion-anion (A-A) and were computed for the [bmim][Cl] at three different temperatures and are shown in Figure 7(a), 7(b), and 7(c).

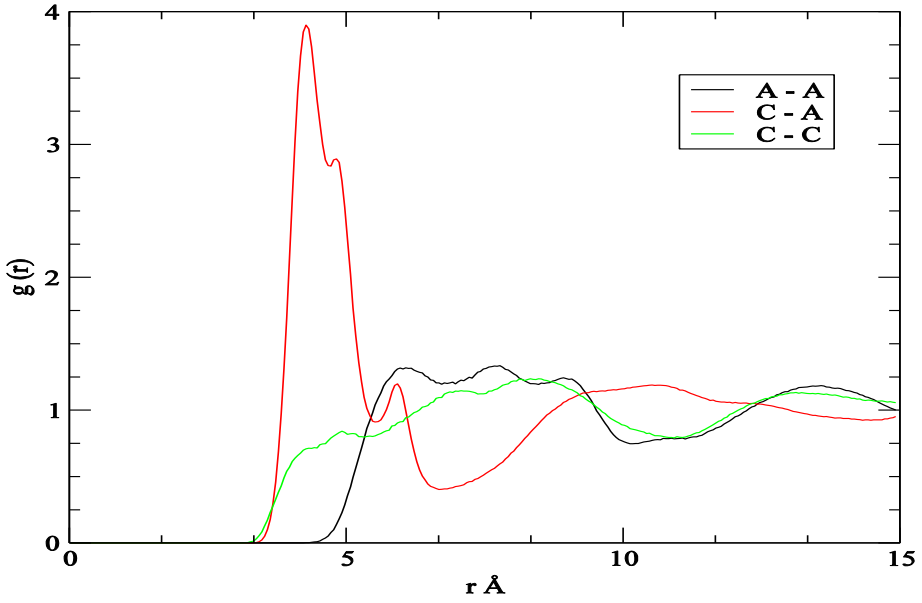

Figure 7: (a) Radial distribution functions of [bmim][Cl] at 293K

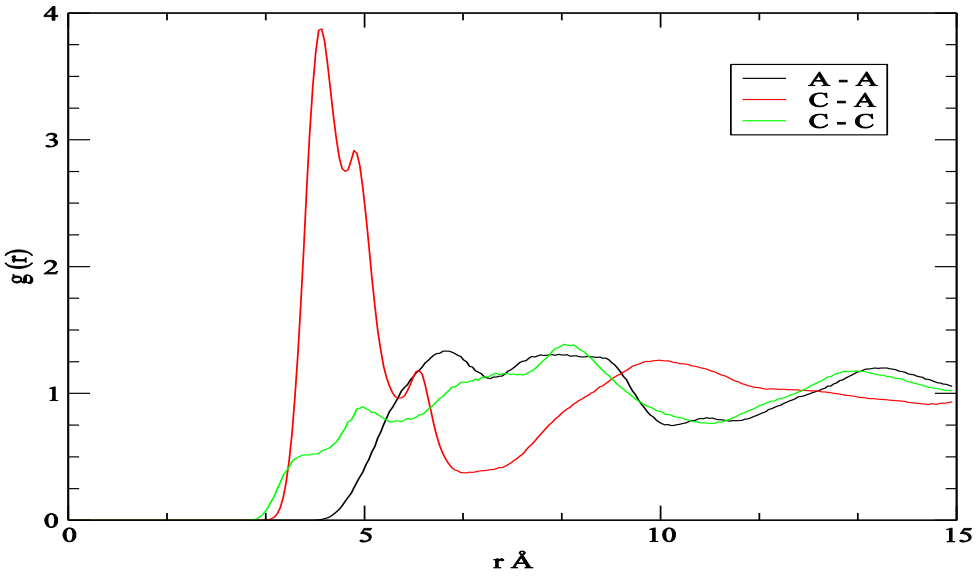

Figure 7: (b) Radial distribution functions of [bmim][Cl] at 300K.

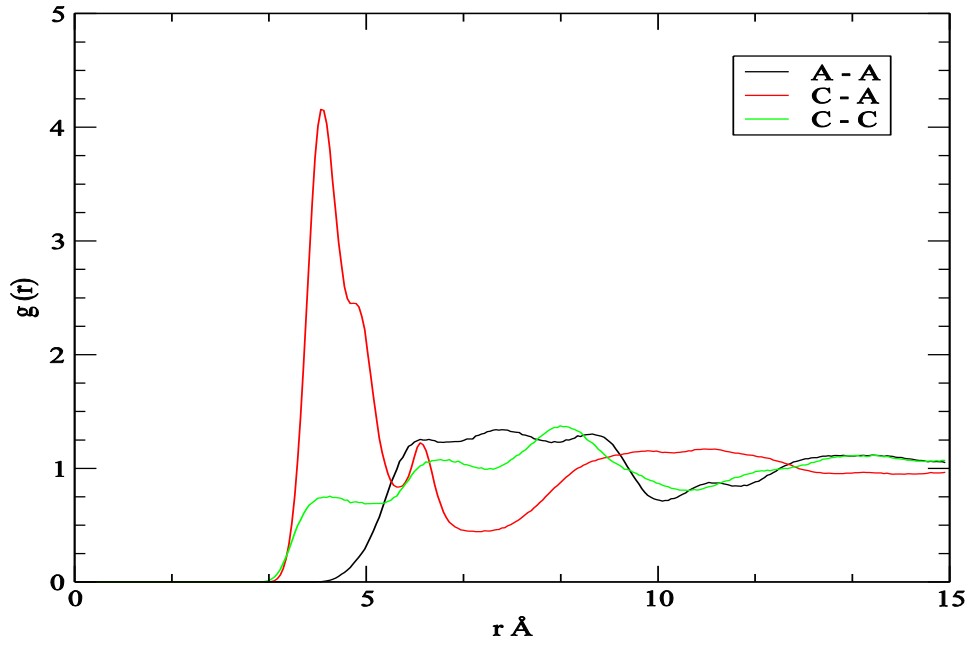

Figure 7: (c) Radial distribution functions of [bmim][Cl] at 308K.

For each case we found that the natures of the RDFs are almost same at different temperature. This is because the temperature range considered in this work is within 20K. Such difference in temperature is small enough to induce variation in RDFs. According to RDFs plot between C-A we found two distinct solvation shells at around 5.5 A^o and 11 A^o respectively. This finding agrees well with other simulation and experimental studies[42]. For each case we found high intense first peak which indicates the central cation is highly surrounded by anions and vice-versa. We further found that the intensity of the first peak increases with increase in temperature. The RDFs for C-C and A-A show oscillations extending beyond 15 A^o. Such charge ordering occurs due to strong long range Columbic interactions of the systems like ILs.

5. CONCLUSIONS

In this thesis an attempt has been made to model a class of ionic salt namely 1-Butyl-3-methylimidazolium chloride ([bmim][Cl]) by using Antechamber code of AMBER[33] force-field. All-atom MD simulation studies were performed by taking 100 of such ion-pairs at three different temperatures such as 293K, 300K and 308K. The density of the compound at different temperatures were calculated and is found to agree well with the available experimental data. We have looked into the structural properties by calculating radial distribution functions (RDFs) between cation-anion (C-A), cation-cation (C-C) and anion-anion (A-A) part of the system. Presence of two distinct solvation layers are evident from the RDFs of C-A. The RDFs of C-C and A-A are found to oscillatory in nature. The results obtained from our study agree well with available X-ray diffraction study.

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